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TRANSLATION

THERMAL DECOMPOSITION AND BURNING OF
AMMONIUM PERCHLORIDE

By

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THERMAL DECOMPOSITION AND BURNING OF AMMONIUM PERCHLORIDE

A. A. Shidlovskiy and L. F. Shmagin

Ammonium perchlorate NH_4ClO_4 was first synthesized by Serullas in 1831 [1]. Since the 1900's it has been used as an oxidizing agent in various explosive, powdered, and pyrotechnical mixtures [2-4]. The production of ammonium perchlorate and the quality of the conduct obtained have been described earlier [5-7].

The physicochemical properties of ammonium perchlorate have been described with sufficient detail in manuals [8, 9] and monographs [2, 7, 10]. The heat of formation ($-\Delta H_{298}$) of crystalline NH_4ClO_4 is indicated as equal to 69.42 kcal/g-mole [11, compare also 12, 13].

Thermal decomposition of ammonium perchlorate was studied by Naoum and Aufschlager [14], Kast [15], Dode [16], Bircumshaw and Newman [17], Bircumshaw and Phillips [18], Galwey and Jacobs [19], Hermoni and Salmon [20], Solymosi and Revesz [21]. The process of its burning (without additions of combustible substitutes) was studied by Adams, Neumen, and Robins [22], Friedman, Nugent, Rumbel, and Scurlock [23], and also by us [24]. In recent years a number of works have appeared in which the burning process of mixtures of NH_4ClO_4 with various organic substances were studied, for example [25]; many of

these works found reflections in literary reviews [26-28].

Our study is a part of an investigation whose end purpose is to explain the mechanism of exothermic decomposition of ammonium salts [24].

EXPERIMENTAL PART

Determination of the flash point of ammonium perchlorate with catalytic additions was performed in a bath filled with Wood's alloy with test tubes inserted into it [29]. The rate of heating the bath was 20° per minute. The sample of NH_4ClO_4 weighed 0.2 g. The results of the determination are shown in Fig. 1.

TABLE 1

Flash Point of NH_4ClO_4 with Catalytic Additions

Catalytic addition	Flash point, °C	Comments
Without addition	> 360	Starting from 270° violent vapors are released; on heating to 360° flashes are not observed
MnO_2—5%	260—270	Light flakes with the appearance of fire
Cu_2Cl_2—5%	290	Same

Combustion of the ammonium perchlorate was done at atmospheric pressure at room temperature in glass tubes with an inside diameter of 22 mm. Compaction of the substance was done by hand with a wooden plunger. The density of the combustible samples varied within 1.10-1.20 g/cm³. The height of the column of the combustible substance in all experiments was from 2.0 to 2.5 cm. Firing was done by a loop of nichrome wire heated by an electrical current (12 v). The burning time was measured by a stopwatch. The amount of the catalytic addition

varied from 10% to 0.5%. As catalytic addition we tested compounds of elements having a variable valence, chromium manganese and copper: $K_2Cr_2O_7$, MnO_2, $KMnO_4$, $CuCl_2 \cdot 2H_2O$, Cu_2Cl_2.

We used ammonium perchloride with 99.25% NH_4ClO_4 which had been passed through a No. 58 sieve. The data obtained are shown in Table 2.

TABLE 2

Burning Velocity of Ammonium Perchlorate with Catalytic Additions

Catalytic addition	Burning time, sec	Burning velocity cm/sec	Comments
Without addition	—	—	Doesn't burn. Violent vapors are released on heating a wire
$K_2Cr_2O_7$—10%	—	—	Same
MnO_2—10%	55	0,042	
	57	0,040	
" 5%	60	0,040	
	55	0,042	
" 3%	—	—	Ignites, but dies out several seconds after switching off intense heat
$KMnO_4$—10%	75	0,029	
	73	0,032	
" 5%	100	0,022	
	98	0,022	
" 3%	—	—	Ignites, but quickly dies out
$CuCl_2 \cdot 2H_2O$—5%	31	0,074	
	33	0,067	
" 3%	49	0,045	
	52	0,044	
" 2%	56	0,041	
	53	0,042	
" 1%	—	—	Ignites, but quickly dies out
Cu_2Cl_2* — 5%	21	0,095	
" 2%	26	0,078	
" 1%	38	0,059	
" 0,5%	70	0,029	Ammonium perchlorate next to lower part of tube walls didn't burn

* All experiments with Cu_2Cl_2 were carried out in tubes with an inside diameter of 34 mm.

As we see from Table 2 under the conditions of our experiment ammonium perchlorate is able to burn when catalysts are added to it: MnO_2, $KMnO_4$, $CuCl_2 \cdot 2H_2O$ and Cu_2Cl_2*. Maximum burning velocity is observed on addition of copper compounds; on addition of Cu_2Cl_2

* New data on the structure of compounds Cu_2Cl_2 and $CuCl_2 \cdot 2H_2O$ are shown in Yu. K. Syrkin study. Uspekhi Khimii, 28, 904 and 918, (1959).

burning is accompanied by the formation of a clearly noted flame. Potassium bichromate (10%) does not make ammonium perchlorate capable of burning under the conditions of our experiments. The addition of a small amount of hydrazine perchlorate [30] to NH_4ClO_4 considerably accelerates the burning process. For example a mixture of NH_4ClO_4 (95%) + $N_2H_5ClO_4$ (5%) with the addition of 5% Cu_2Cl_2 (over 100%) stably burns in a tube with a diameter of 2.5 mm at a velocity of about 0.22 cm/sec.

The addition of any combustible to ammonium perchlorate sharply increases the heat and temperature of the reaction. We prepared a mixture of ammonium perchlorate with glucose in a ratio of 80 : 20 which corresponds to the stochiometric ratios. It was assumed that the reaction should occur according to the equation:

$$6NH_4ClO_4+C_6H_{12}O_6=6CO_2+18H_2O+3N_2+3Cl_2.$$

The calculated heat of this reaction was 995 kcal/kg.

The results of burning this mixture as such and with the addition of a catalyst are shown in Table 3.

TABLE 3

Burning of Mixture: Ammonium Perchlorate (80%) + + Glucose (20%) (Tube Diameter 10 mm)

Catalytic addition	Column height, mm	Density, g/cm³	Burning time, sec	Burning velocity, cm/sec
Without addition	11	1,33	18	0,061
	15	1,27	23	0,065
$CuCl_2\cdot 2H_2O$ — 5%	15	1,29	16	0,097
	14	1,34	13	0,105
Cu_2Cl_2 — 5%	12	1,33	9,8	0,125
	12	1,28	9,6	0,123

It is interesting that the addition of glucose which sharply increases the heat and temperature of burning comparatively little

increases the burning velocity of the system (compare, for example, 0.095 mm/sec in Table 2 and 0.12 mm/sec in Table 3).

It is possible that burning of mixtures of ammonium perchlorate with organic substances occurs in two stages: at first burning of the oxidizing agent itself and then oxidation of the organic substances by the decomposition products of the oxidizing agent similar to that which takes place for mixtures of ammonium nitric with organic substances [31].

CONCLUSIONS

1. Catalytic additions of compounds of elements with a variable valence, namely: Cu_2Cl_2 and MnO_2, considerably lower the flash point of the ammonium perchlorate.

2. Ammonium perchlorate without additions does not burn at atmospheric pressure, room temperature, and tube diameter of 22 mm. It acquires the ability to burn under these conditions when we add to it not less than 5% MnO_2 or $KMnO_4$, not less than 2% $CuCl_2 \cdot 2H_2O$, or not less than 0.5% Cu_2Cl_2 (the last addition was tested with a tube diameter of 34 mm).

3. The addition of 20% glucose to ammonium perchlorate (with a catalytic addition of Cu_2Cl_2) only slightly increases its burning velocity. This fact indicates that the leading process is the burning of ammonium perchlorate as an individual substance, whereas oxidation of the combustible substances is a secondary process accomplished by the combustion products of ammonium perchlorate.

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